icals, all of our previous measurements[16,20–22] are quantitatively consistent with the assumption that the presence of oxygen has no influence on the reactivity of iodine atoms. In the present system, exchange proceeding by the iodine abstraction mechanism is subject to oxygen inhibition of step (A2), while exchange proceeding by the direct substitution mechanism (S1) should be unaffected. The major conclusions of this study would be supported by the presence of a residual exchange reaction whose rate remained constant over a considerable range of partial pressures of oxygen. However, since the concentration of oxygen could not be increased sufficiently for it to compete with the suggested reaction of butyl radicals with iodine molecules formed at their own geneses,[23] the oxygen effect would not of itself distinguish between the alternative explanations of the high ratio of racemization to exchange.

Acknowledgment.—This work was supported in part by the U. S. Atomic Energy Commission under Contract No. AT(30-1)-1314.

Some of the final calculations were completed at the University of Leeds while the senior author was holding a fellowship from the John Simon Guggenheim Memorial Foundation.

We are grateful to Professor C. E. H. Bawn of the University of Liverpool for pointing out to us that the oxygen effect discussed in the last paragraph would not distinguish between substitution with inversion of carbon and reaction of butyl radicals and iodine molecules produced simultaneously.

NEW YORK 27, N. Y.

[21] D. J. Sibbett and R. M. Noyes, THIS JOURNAL, **75**, 763 (1953).

[22] F. W. Lampe and R. M. Noyes, *ibid.*, **76**, 2140 (1954).

[23] R. M. Noyes, *ibid.*, **77**, 2042 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

The Decomposition of Thiourea in Water Solutions

BY WILLIAM H. R. SHAW AND DAVID G. WALKER[1,2]

RECEIVED JUNE 13, 1956

Rate measurements were made at various thiourea concentrations ranging from 5 to 960 millimolar. The reaction was shown to be first order with respect to thiourea. Runs were also made in media containing various acids and salts. The reaction rate was found to be independent of acid concentration over a wide range and did not depend on ionic strength. Data collected at 10° temperature intervals from 90 to 130° were analyzed and a frequency factor and activation energy are reported. A discussion of these and other findings is presented.

Introduction

In a stimulating account of his pioneering researches, Reynolds[3] first reported the synthesis of thiourea and its isomerization to ammonium thiocyanate. Kinetic studies of the reaction in the absence of solvent have been made by Waddell,[4] Atkins and Werner,[5,6] Kappanna,[7] and Kodama, *et al.*[8] Ure and Edwards[9] have investigated the reaction with ethylene glycol as a solvent. The only moderately extensive data on the decomposition of thiourea in aqueous media that could be found in the literature were reported by Dutoit and Gagnaux[10] although scattered information from various sources is also available. Studies on the phase relationships[11–13] and the equilibrium[5–7,12,13] between thiourea and ammonium thiocyanate have been made in the absence of solvent. This equilibrium has also been investigated in water,[5,10] simple alcohols[5,13] and ethylene glycol.[14] A recent study of the effect of pressure[15] on the kinetics of this reaction and the position of equilibrium in the absence of solvent should also be mentioned.

Data on the decomposition of urea in aqueous media have been presented in a previous communication[16] from this Laboratory. The reaction was shown to be first order with respect to urea over a wide concentration range. No significant salt effects were observed and the decomposition reaction was not catalyzed by any of the common inorganic acids tested. The products of the reaction in the absence of acid were ammonium ions and cyanate ions.

Since no complete data on the kinetic behavior of thiourea in aqueous solutions could be found in the literature, the present investigation was undertaken with two objectives in mind: to collect such data, and to compare the findings with those previously obtained with urea. It was hoped that such a comparison might provide clearer insight into the mechanisms of both reactions.

Experimental

Apparatus and Technique.—Aqueous solutions of thiourea were sealed in glass ampoules and placed in an oil-bath maintained at the reaction temperature. After 15 min. blanks were withdrawn and quenched in water. The remaining ampoules were left in the bath for reaction periods varying from 3 to 48 hr. In the equilibrium studies

---

[1] Presented before the Division of Physical and Inorganic Chemistry, 8th Southwest Regional Meeting of the American Chemical Society held in Houston, Texas, December, 1955.

[2] *Chem. Eng. News*, **34**, 340 (1956).

[3] J. E. Reynolds, *J. Chem. Soc.*, **22**, 1 (1869).

[4] J. Waddell, *J. Phys. Chem.*, **2**, 525 (1898).

[5] W. R. G. Atkins and E. A. Werner, *J. Chem. Soc.* (*London*), *Trans.*, **101**, 1167 (1912).

[6] Ref. 5, **101**, 1982 (1912).

[7] A. N. Kappanna, *J. Indian Chem. Soc.*, **4**, 217 (1927).

[8] S. Kodama, *et al.*, *J. Chem. Soc. Japan, Ind. Chem. Soc.*, **56**, 49 (1953); *C. A.*, **48**, 8000 (1954).

[9] W. Ure and T. B. Edwards, *Trans. Roy. Soc. Canada*, **24**, Sec. III 153 (1930).

[10] P. Dutoit and L. Gagnaux, *J. chim. phys.*, **4**, 261 (1906).

[11] A. Findlay, *J. Chem. Soc.* (*London*), *Trans.*, **85**, 403 (1904).

[12] J. E. Reynolds and E. A. Werner, *ibid.*, **83**, 1 (1903).

[13] G. H. Burrows, THIS JOURNAL, **46**, 1623 (1924).

[14] W. Ure and F. A. DeLisle, *Trans. Roy. Soc. Canada*, **27**, Sec. III, 105 (1933).

[15] T. Yanagimoto, *Rev. Phys. Chem. Japan*, **24**, No. 1, 1 (1954).

[16] W. H. R. Shaw and J. J. Bordeaux, THIS JOURNAL, **77**, 4729 (1955).

lasting 24 or 80 days an oven was used in place of the oil bath. A more detailed description of the apparatus and technique has been presented previously.[16]

Analytical Methods.—After reaction the samples were analyzed for ammonium ion by essentially the same procedure employed in earlier work.[16–18] It was necessary, however, to wash the ion-exchange column very carefully to remove the last traces of thiourea before eluting the ammonium ion. Unless it is quantitatively removed, thiourea reacts with the Nessler reagent and makes analysis impossible. By careful washing, or by adsorbing, washing, eluting, re-adsorbing, washing, eluting and analyzing, it is possible to determine ammonium ion at the 0.1 millimolar level in the presence of thiourea at the 1 molar level with an average deviation of from 2–3%.

Thiocyanate ion was determined spectrophotometrically[19] by adding standard ferric nitrate to the reaction mixture and measuring the absorbance with a Beckman Model B spectrophotometer. Comparison with a standard curve of absorbance *vs.* thiocyanate concentration was then made and the concentration of thiocyanate in the reaction mixture calculated. In reaction media containing added salts, acids or bases, extensive measurements were made to establish the presence or absence of interference by these substances. If interference was encountered, a new standard curve was constructed using solutions of known thiocyanate concentrations containing the interfering substance at the same concentration employed in the run. If this technique gave erratic results, no thiocyanate analysis was reported. The average deviation of a set of 14 independent analyses of 0.060 *M* thiocyanate solution was 2.8%.

Thiocyanate plus thiourea was occasionally determined as a cross-check on the data by titration with standard mercuric nitrate using ferrous ammonium sulfate as an indicator.[7]

Reagents.—Fischer Scientific Company certified reagent grade thiourea, m.p. 179°, was used without further purification. Distilled water that had been passed through a large capacity Dowex 50 cation exchanger was employed in the preparation of solutions. All other chemicals employed in the work were of analytical reagent grade and conformed to A.C.S. specifications.

Results

In the absence of acids and bases it was found possible to account quantitatively for all products by the equation

$$CS(NH_2)_2 \xrightarrow{k_1} NH_4^+ NCS^- \qquad (1)$$

For this reaction, assumed to be first order, it follows that

$$-du/dt = k_1 u \qquad (2)$$

$$u_d/t = k_1 \bar{u} \qquad (3)$$

where u is the thiourea concentration, u_d the thiourea decomposed in reaction time t, and $\bar{u}$ the average thiourea concentration. Attention was next directed to a proof of the applicability of equation 3 to the thiourea decomposition.

In general, less than 1% of the thiourea present initially reacted; and, consequently, it did not differ significantly from the initial thiourea concentration. The thiourea decomposed was measured by determining the thiocyanate concentration and ammonium concentration produced at the end of the reaction time. On the basis of these observations u_d *vs.* t plots were constructed and resulted in essentially superimposable straight lines passing through the origin.

The order of the reaction was then determined by plotting rate (u_d/t) against $\bar{u}$. A straight line passing through the origin was obtained and a first-order dependence of rate on thiourea concentration was, consequently, established. Results obtained at different temperature and rate constants calculated on the basis of equation 3 are recorded in Table I. Data collected in media of varying ionic strength (Table II) and those obtained with different acids and at high *p*H in borate buffers are summarized in Fig. 1. Results of an equilibrium study are presented in Table III.

TABLE I

FIRST-ORDER RATE CONSTANTS AT VARIOUS TEMPERATURES

Temp., °C. ±0.05	Thiourea × 10^3, *M*	Reaction time or range, hr.	No. of determinations	$k \times 10^8$, sec.$^{-1}$
90.0	15–240	24.4	10	4.53 ± 0.17[a,b]
100.0	30–960	11.5–44.3	24	17.0 ± 0.5[c]
110.0	60–960	5.0	10	59.3 ± 1.7[c]
120.0	60–475	3.15	8	197 ± 8[b]
130.0	60–960	0.90–0.91	10	613 ± 10[b]

[a] Average deviations. [b] Based on NH_4^+ analysis alone. [c] Based on NH_4^+ analysis and SCN^- analysis.

TABLE II

THE EFFECT OF ADDED SALT[a]

Salt	Ionic strength, moles/l.	Reaction time, hr.	$u_d(NH_4^+)$,[b] moles/l. × 10^3	k_1, sec.$^{-1}$ × 10^7
None[c]	10^{-4}	44.25	1.59	1.69
NaCl	2	44.25	1.60	1.69
$NaNO_3$	2	44.25	1.63	1.72
Na_2SO_4	2	44.25	1.58	1.67
NaCl	1	36.0	1.31	1.69
$NaNO_3$	1	36.0	1.33	1.72
Na_2SO_4	1	36.0	1.28	1.67

[a] Runs were made at 100.0 ± 0.05° at an initial thiourea concentration of 0.060 *M*. [b] The high salt concentration prevented thiocyanate analysis. [c] This represents an approximate value of the average ionic strength of the ammonium thiocyanate produced in the reaction.

TABLE III

EQUILIBRIUM DATA[a]

Initial sample compn., *M* × 10^3		Time at 100°, days	Final sample compn., *M* × 10^3			Equilibrium % thiourea
NH_4-SCN	$CS(NH_2)_2$		SCN^-	NH_4^+	$SCN^- + CS(NH_2)_2$	
63.4	0.00	24	62.3	..	63.4	1.7
57.6	0.00	24	56.0	..	57.6	2.7
0.00	60.0	80	58.6	58.4	..	2.3
0.00	60.0	80	58.4	..	..	2.7

[a] This equilibrium has been studied previously in water,[5] ethylene glycol,[13] butyl and propyl alcohol[14] and in the absence of solvent.[3,4,7] The equilibrium percentages of thiourea ranged from 33.5 to 21% in the absence of solvent over a temperature range of 132–180°. Data in butyl and propyl alcohol did not differ significantly from these values while other work in ethylene glycol and water[5] gave equilibrium percentages of thiourea from 2–4% in the temperature range 142–184°.

Discussion

An examination of Fig. 1 reveals that the decomposition of thiourea in aqueous media is independent of hydrogen ion concentration over an extremely wide range. The experimental first order constant based on the rate of production of thiocyanate remains constant in media of high *p*H, neutral solutions, and solutions of moderate acid concentra-

---

[17] G. B. Kistiakowsky, P. C. Mangelsdorf, A. J. Rosenberg and W. H. R. Shaw, THIS JOURNAL, **74**, 5015 (1952).

[18] W. H. R. Shaw and J. J. Bordeaux, *Anal. Chem.*, **27**, 138 (1955).

[19] F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. II, Third Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1948, p. 783.

tion. In concentrated acid solutions, however, the thiocyanate ion begins to hydrolyze to ammonium ion.[20] Other complicating side reactions probably are involved also.[21]

The rate based on the production of ammonium ion shows an interesting deviation from the thiocyanate rate in solutions above *p*H 7. This increase in rate can be explained by assuming the onset of a base-catalyzed parallel reaction that does not produce thiocyanate. A possible reaction sequence involves

$$OH^- + CS(NH_2)_2 \longrightarrow SH^- + CO(NH_2)_2 \quad (4)$$

$$CO(NH_2)_2 \longrightarrow NH_4^+ + CNO^- \quad (5)$$

Reaction 4 might take place directly or through the intermediate formation of cyanamide.[22] It is interesting to record that treatment of reaction mixtures with mercuric nitrate gave no precipitate in the *p*H 7 and 7.5 samples but a black precipitate was formed in all samples of higher *p*H. Precipitation became increasingly pronounced with increasing *p*H. The compounds formed by mercuric ion and thiourea are slightly soluble and are not precipitated under the test conditions used. These observations indicate that, as a tentative hypothesis, reactions 4 and 5 or a similar scheme can be formulated to explain the appearance of sulfide ion and the simultaneous formation of excess ammonium ion. It appears, therefore, that aside from complicating reactions at the extreme *p*H's studied, the decomposition of thiourea is *p*H independent. Free hydrogen ions and hydroxide ions are not involved in the rate-determining step.

Ionic strength has no detectable influence on the rate (Table II), but unless a rather large difference in dipole moment existed between the activated complex and the reactant no measurable effect would be expected in water solutions at the temperatures studied.[23] It is interesting to point out that because of the very high dipole moments of urea and thiourea[24] it is possible that the activated complexes involved in the decompositions of these molecules may be less polar than the reactants. The approximate analysis previously presented[16] is, consequently, not necessarily valid.

Data obtained by other investigators is presented in Table IV. It is apparent that change in solvent has no drastic effect on the reaction rate. The activation energies and frequency factors reported by most investigators (Table IV) are essentially identical. The early work of Dutoit and Gagnaux[10] is the only exception. These investigators have pointed out that the glass reaction vessels used in their work were attacked by the experimental solutions. The effect depended on the reaction time. At low temperatures, reaction times were quite long and a precipitate containing 50% silica was formed. The viscosity of these solutions was "enormously increased."[10]

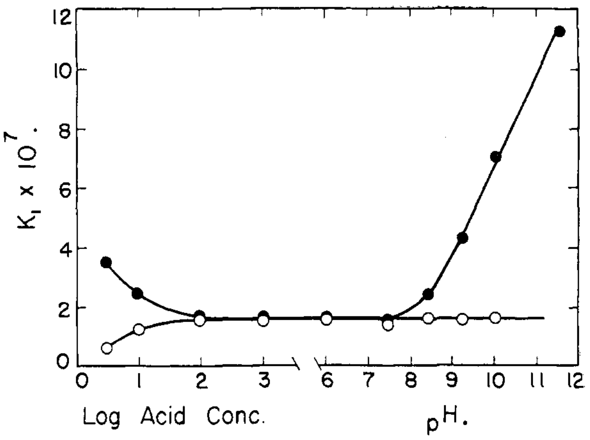


Fig. 1.—Observed first-order rate constants based on NH_4^+ analysis (●) and thiocyanate analysis (O) as a function of acid concentration. Runs above *p*H 7 were made in 0.00125 *M* borax solutions. Results recorded below *p*H 7 were based on data collected for HCl. Other data obtained with HNO_3, H_2SO_4 and H_3PO_4 did not differ significantly from the plotted values. All runs were made at 100.0 ± 0.05° at an initial thiourea concentration of 0.060 *M*.

TABLE IV

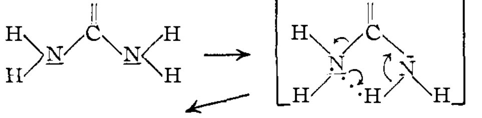
ARRHENIUS PARAMETERS FROM VARIOUS SOURCES[d]

Medium	Frequency[a,b] factor, sec.$^{-1}$	Activation[a,b] energy, kcal.	Temp. range, °C.	Ref.
Water	3.60×10^{16} (5.75×10^{16})	40.5 (40.9)	148-76	10
Melt[c]	1.25×10^{14} (2.62×10^{14})	35.0 (35.5)	140-80	7
Melt[c]	4.82×10^{13} (9.1×10^{13})	34.0 (34.4)	150-90	8
Water	1.53×10^{14}	35.8	90-130	This work[e]

[a] Unparenthesized values are those reported by the original investigators. [b] Values in parentheses are recalculated from the raw data by a least squares analysis. [c] Molten mixtures of NH_4SCN and $CS(NH_2)_2$. [d] This table summarizes all available rate data from the literature except those obtained in ethylene glycol[9] at 178 and 184° and scattered data[4,5] obtained in the absence of solvent. [e] These parameters will reproduce the rate constants of Table I to within 3% and will also reproduce the other rate constants[10] reported in water within 25%.

In the absence of solvent and in ethylene glycol the synthesis of thiourea from ammonium thiocyanate is described[4-9] as a unimolecular first-order reaction. This behavior is in sharp contrast with the second-order synthesis of urea from ammonium cyanate observed in water.[25] No data on the kinetics of the thiourea synthesis in aqueous media are available, but it is highly probable that second-order kinetics would be found. Further work on this point is clearly indicated.

In the light of available information a plausible reaction mechanism for the decomposition of thiourea might be formulated as


(I)

$$NH_3 + HNCS \rightleftarrows NH_4^+ + NCS^- \quad (II)$$

---

(20) J. N. Friend, "A Textbook of Inorganic Chemistry," Vol. VII, Charles Griffin & Co., London, 1931, p. 281.

(21) R. H. Sahasrabudey and R. Singh, *J. Indian Chem. Soc.*, **30**, 500 (1953).

(22) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 340.

(23) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., p. 141.

(24) W. D. Kumler and G. M. Fohler, THIS JOURNAL, **64**, 1944 (1942).

(25) Ref. 23, pp. 257-265.

The equilibrium in the second step should lie far to the right in aqueous solutions since HNCS unlike HNCO is a strong acid.[26] Such an equilibrium can be used to explain the very low yields of thiourea from ammonium thiocyanate obtained in water solutions (Table III).

Formation of the activated complex in Step I is assumed to involve the partial intramolecular transfer of a hydrogen ion from one nitrogen atom to the next. This step can be rationalized by assuming an attraction of the embryonic proton on N by the unshared electron pair on N′. Examination of models also reveals that a hydrogen atom on N is close enough to the unshared pair on N′ to experience relatively easy transfer. Since the mechanism assumes an intramolecular hydrogen transfer, the reaction rate should not be influenced by *p*H.

The observed frequency factor in water is slightly larger than ekT/h indicating a positive entropy of activation[27] of about 3.9 e.u. Reactions in the gas phase involving a cyclic activated complex, however, proceed with a negative entropy of activation. In view of the high dipole moment of thiourea it is possible that the activated complex is less polar than the reactant. Formation of a less polar activated complex from the solvated dipolar reactant could, consequently, lead to the release of bound solvent molecules to begin a more random existence in solution. Such an increase in entropy could more than balance the orderliness conferred by the formation of a cyclic activated complex. A detailed analysis of this point must await the collection of more comprehensive data on the reaction in different solvents.

It is interesting to note that, aside from the slightly positive entropy of activation, the reaction studied in this work has many features in common with so-called "four-center reactions."[28] The mutually similar features include: involvement of four key atoms, little effect of solvent, no requisite acid or base catalysis, etc.[28]

The products obtained by the thermal decomposition of substituted thioureas now under investigation in this Laboratory can be predicted by assuming an intramolecular hydrogen transfer from nitrogen to nitrogen. This finding, if completely confirmed, can also be used to rationalize the postulated mechanism or establish a more satisfactory one.

Acknowledgment.—The authors gratefully acknowledge the generous grant from Research Corporation of New York that made this study possible.

---

(26) H. E. Williams, "Cyanogen Compounds," Edward Arnold and Co., London, 2nd Edition, 1948, p. 309.

(27) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 417.

(28) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1956, pp. 453-465.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Interaction between Methyl Borate and Amines as Evidenced from Vapor Pressure Studies

BY HERMAN HORN AND EDWIN S. GOULD

RECEIVED JULY 2, 1956

Mixtures of methyl borate and a number of aliphatic and heterocyclic amines have partial vapor pressures of methyl borate substantially less than would be calculated for ideality. The partial vapor pressures of methyl borate over a number of such mixtures have been measured and the departures from ideality, which should reflect the degree of amine-borate interaction, have been tabulated. Studies have been extended to systems containing the third component, methanol. Interaction is greatest for the difunctional amines, piperazine and ethylenediamine and for triethanolamine. It is least for trimethylamine, di-*i*-propylamine and pyridine. The role of methanol, which markedly increases the apparent amine-borate interaction in some cases, but not in others, is still not clear.

Interaction between methyl borate and amines varies markedly with the structure of the amine. At one extreme are methylamine,[1] ethylenediamine[2] and triethanolamine, which rapidly form solid and readily isolable addition compounds. At the other extreme are pyridine, triethylamine and diisopropylamine, none of which appear to interact with methyl borate at room temperature, even on long standing. In intermediate cases, the partial pressures of methyl borate over mixtures of amine and borate have been found to be substantially lower than would be predicted from Raoult's law. Since this departure from ideality is, in a sense, a measure of amine-borate interaction, we here compare the partial vapor pressures of methyl borate over a number of such mixtures to those partial pressures expected for ideal solutions. Dissociation constants of the addition compounds in the vapor state could not be obtained by gas density measurements since association appeared to be measurable only at temperatures slightly above the condensation points where departure from the ideal gas law is appreciable. The dissociation pressures of the solids themselves cannot be readily converted to thermodynamic dissociation constants since the vapor in equilibrium with the solid addition compounds does not necessarily have the same composition as the solid (*i.e.*, the addition compounds may exist as solids over a *range* of compositions at temperatures where both components are liquid when alone).

Because the interaction between methyl borate and some amines was found to be affected by added methanol,[2] vapor pressure studies were extended

---

(1) J. Goubeau and R. Link, *Z. anorg. Chem.*, **267**, 27 (1952).

(2) S. V. Urs and E. S. Gould, THIS JOURNAL, **74**, 2948 (1952).